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ENERGY AND TANGENTIAL MOMENTUM ACCOMMODATION ON

DIFFERENT FLASHED TUNGSTEN AND GAS COVERED TUNGSTEN SURFACES

by

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The University of Mississippi
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
The acoustical method has been used to determine energy and tangential momentum accommodation coefficients on three different polycrystalline tungsten surfaces. To obtain the second surface, the first was highly oxidized and then cleaned by vacuum flashing at $2150°K$. The third surface, manufactured by the same chemical deposition process as the first, was specified as having $\frac{1}{2}$ the microscopic roughness of the first. Photographs made with the scanning electron microscope indicate that though the oxidation dramatically increased the roughness of the surface, this roughness was removed in the flashing process. (cont. on next page)

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The electron micrographs also showed that flashing dramatically increased the grain size in the third surface. This third surface, though supposedly smoother, was found to have larger AC values than the first. This has been attributed to a shorter accumulated flashing time at the time the measurements were made and, therefore, smaller grain size. The microscopic roughness does not appear to be an important factor in determining AC values after the surface is flashed.

The problem of simultaneously determining energy and tangential momentum accommodation coefficients is discussed.

The sum of the energy (EAC) and tangential momentum (TMAC) coefficients has been measured acoustically for Ne on W exposed to the following adsorbates: CO, CO_2, O_2, N_2, H_2O and D_2; for He on W with O_2 and D_2 as adsorbates; and for each of these adsorbates on itself on W. An effort has been made to infer separate values of EAC and TMAC from the measured values of their sum. Good agreement is obtained with EAC values obtained from thermal conductivity cell measurements if TMAC is assumed to have a value of 0.75 for He and Ne on all the gas covered surfaces and a value of 1.0 for all the adsorbates except D_2 on itself on W. The acoustical method which was used has the unique capability of determining AC values under gas dynamic conditions where the surface and the gas are at essentially the same temperature. For CO_2, since the acoustical measurements were made at frequencies far above the vibrational relaxation frequency, the EAC value obtained is for the translational and rotational energy only. The measurements in D_2 reveal rotational relaxation.

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PART I

ENERGY AND TANGENTIAL MOMENTUM ACCOMMODATION COEFFICIENTS OF

NEON AND HELIUM ON DIFFERENT VACUUM FLASHED TUNGSTEN SURFACES

Abstract

The acoustical method has been used to determine energy and tangential
momentum accommodation coefficients on three different polycrystalline
tungsten surfaces. To obtain the second surface, the first was highly
oxidized and then cleaned by vacuum flashing at 2150°K. The third sur-
face, manufactured by the same chemical deposition process as the
first, was specified as having ½ the microscopic roughness of the first.
Photographs made with the scanning electron microscope indicate that
though the oxidation dramatically increased the roughness of the sur-
face, this roughness was removed in the flashing process. The electron
micrographs also showed that flashing dramatically increased the grain
size in the third surface. This third surface, though supposedly
smoother, was found to have larger AC values than the first. This has
been attributed to a shorter accumulated flashing time at the time the
measurements were made and, therefore, smaller grain size. The micro-
scopic roughness does not appear to be an important factor in determin-
ing AC values after the surface is flashed.

The problem of simultaneously determining energy and tangential
momentum accomodation coefficients is discussed.

1.   INTRODUCTION

In the summer of 1974, energy and tangential momentum accommoda-
tion coefficients were first obtained from the measurement of the
velocity and absorption of sound waves propagated through rarified
gases confined to a tube[1]. For many years it had been known that
energy accommodation coefficients for gaseous molecules striking a
metal surface dropped dramatically when adsorbed molecules were
removed from the surface. The acoustic measurements showed that tan-
gential momentum accommodation coefficients had a similar dramatic
decrease.

At about the same time the acoustic experiments were being per-
formed, R.G. Lord and L.B. Thomas made a similar discovery by measuring
the drag on a vane rotating in gases at reduced pressures[2]. In 1976,
Steinheil, Scherber, Seidl, and Rieger reported similar dramatic
decreases in momentum accommodation when contaminants were removed from
a gold surface. Their measurements were made using a molecular beam
apparatus[3].

The work reported here is divided into two parts. The first part
discusses the problems involved in uniquely determining both the energy
accommodation coefficient (EAC) and the tangential momentum accommoda-
tion coefficient (TMAC) from sound velocity and absorption measurements.
The second part reports measurements comparing the AC values for three
different tungsten surfaces. Each surface was cleaned before measure-
ments were made on it by flashing at approximately 2150°K in a vacuum
in the presence of mischmetal getter. AC values for the first surface
were reported in 1975 and have been checked with modified apparatus in

1979 and 1981. The second surface measured was produced by exposing

the first surface briefly to the atmosphere while the surface was at

approximately 2150°K and then subsequently flashing the surface in a

vacuum at 2150°C. The third surface was similar to the first but was

specified by the manufacturer as having a roughness factor approxi-

mately one-half as large. Scanning electron microscope photographs

have been made of the surfaces.

II. THE PROBLEM OF DETERMINING BOTH EAC AND TMAC FROM ACOUSTIC MEASUREMENTS

While the acoustic method of measuring EAC and TMAC does not allow

the characterization of the surface under investigation to the degree

possible with molecular beam experiments and thermal conductivity ex-

periments, it does offer certain advantages. In the first place, it

allows the measurements to be made with the gas and the surface near

thermal equilibrium. This is not possible for most other methods. In

thermal conductivity measurements of EAC, for example, the surface must

always be hotter than the gas.

Even more important is the unique possibility, at least in princi-

ple, of determining EAC and TMAC simultaneously. In the acoustic meth-

od, a sound wave is propagated through a rarified gas contained in a

tube with a diameter that is a fraction of the sound wavelength. The

absorption and velocity of the sound are sensitive functions of the

temperature jump and velocity slip at the tube wall. These, in turn,

are functions of EAC and TMAC[1]. The two coefficients have similar but

not identical effects upon the absorption and velocity. The experimen-

tal measurements determine the sum of the two (EAC + TMAC) with an ac-

curacy of a few percent. However, the measurements must be very accurate

if the two are to be determined separately. To determine EAC and TMAC a computer is programmed to calculate theoretical values of the sound absorption and velocity and compare these with measured values. The computer then varies EAC and TMAC to obtain the best agreement between the calculated and measured values. Figures 1A and 1B have been drawn to indicate the sensitivity of the theoretical curves to variations in EAC and TMAC. In the absence of relaxation, the propagation constant for the sound waves can be shown to be a function of the ratio of specific heats (γ) and of two dimensionless parameters: r_ω and r'. ($r_\omega = c_0^2 \rho_0 / \omega \eta$ and $r' = r\omega/c_0$, where c_0 is the ideal gas free space sound velocity, ρ_0 is the equilibrium density, ω is the angular frequency, η is the viscosity, and r is the tube radius)[1]. In the measurements reported here, the frequency is held almost constant and the pressure varied. The measured values are corrected for the slight variations in frequency so that the results can be plotted as a function of r_ω for a fixed value of r'.

In Figs. 1A and 1B the theoretical values of the reduced absorption ($\alpha\omega/c_0$) and the inverse of the reduced sound velocity (c_0/c) (these are the real and imaginary parts of the reduced propagation constant) are plotted as a function of r_ω for various values of EAC and TMAC. In these figures, the group of curves lettered A are for EAC + TMAC = 0.6, and those lettered B are for EAC + TMAC = 1.2. For both groups, r' has the value 1.14 and $\gamma = 1.667$, corresponding to that for Ne at 17.8 kHz - the approximate frequency at which the present measurements were made.

Within each group of curves, curve 1 has EAC = TMAC and curve 2 has EAC = 0.2 TMAC. In the computer search for the best values of EAC

and TMAC, it has been assumed that EAC ≤ TMAC. This assumption is made since it seems logical that a polycrystalline surface would scatter some molecules elastically but diffusely. The experimental absorption and velocity curves in helium clearly support this assumption. It should be noted, however, that in some cases (Xe and A⁻ on Ag, for example)[4], molecular beams are scattered supraspecularly. It is conceivable that this could result in EAC being greater than TMAC.

By examination of Figs. 1A and 1B, one sees the kind of accuracy needed in measured values to determine EAC and TMAC separately. For measurements in He, r′ is lowered to 0.51 (at 17.8 kHz). In this case, the variation of the ratio EAC/TMAC has a greater effect upon the theoretical curves, but, unfortunately, the scatter in the experimental measurements in the lighter gas is also greater.

III. COMPARISON OF DIFFERENT TUNGSTEN SURFACES

Measurements reported in the two earlier papers[1,5] were on a single tungsten tube 0.953 cm inside diameter. The tube was manufactured by the Ultramet Company by chemical deposition of tungsten from tungsten fluoride gas on a stainless steel rod. Impurities, including carbon, were estimated to be less than a few parts per million. The stainless steel surface upon which the tungsten was deposited was specified as having a 10 microinch finish (i.e., 0.7 times the average peak to valley difference equals 10 μinches). According to the manufacturer, the crystal growth in the deposition process was such that the 110 crystal plane was perpendicular to the tube surface. However, the inner surface,

which was in contact with the stainless rod in the deposition process, was expected to have a random crystal orientation.

Before trying to extend the measurements to other gases and other metal surfaces, it was deemed desirable to see how the results are affected by variations in the tungsten surface. One such variation was supplied by accident at the conclusion of the measurements reported in Reference 5. The glass envelope of the vacuum system broke while the tungsten tube was being flashed at approximately 2150°K. The surface of the tube was highly oxidized. The oxide on a small piece of this tube was removed by heating it in a hydrogen atmosphere to approximately 1400°K. Fig. 2A shows an electron micrograph of the surface of the piece cleaned in this way.

Figure 3 shows plotted as circles the measurements made using this tube after it was oxidized and subsequently cleaned by flashing at approximately 2150°K in a vacuum of about 10^{-7} Torr and in the presence of mischmetal getter. The gas measured was Ne. The solid curves in the figures are theoretical curves calculated using the EAC and TMAC values published in 1975 for this surface before it was oxidized (EAC = 0.12, and TMAC = 0.53). The sound absorption and velocity measurements indicate that the oxidation – and – subsequent– flashing process has produced little change in the accommodation coefficients. The "best fit" values of EAC and TMAC for the combined absorption and velocity data as selected by the computer were 0.12 and 0.56.

After these measurements and those reported in the following paper, an electron micrograph was made of another piece of this tube. This photograph is shown in Fig. 2B. Comparison of the two photographs (2A and 2B) shows that the vacuum flashing at 2150°K has produced a striking change in the surface.

As a further test of the effect of variations in the tungsten surface, measurements have been made upon a second tube. This tube, manufactured by the same process as the first, was specified by the manufacturer as having half the roughness (i.e a 5 microinch finish). A piece of tube with this surface finish was also heated to 1400°K in a hydrogen atmosphere and then photographed with the scanning electron microscope. The electron micrograph of this surface is shown in Fig. 2C. Measurements made with this second tube after it was vacuum flashed as the first are plotted as x's in Fig. 3. Measurements were also made for this tube using He and are shown plotted in Fig. 4. Again in this figure the solid curves are theoretical curves calculated using EAC and TMAC values measured in 1975 for the smoother tube (EAC = 0.06 and TMAC = 0.38). This time the data for both Ne and He indicate a very definite increase in EAC and TMAC. The computer best fit values for this new tube are for Ne, TMAC = 0.65, EAC = 0.20; and for He, TMAC = 0.52 and EAC = 0.08. In order to be sure that this increase in AC values for the second tube was not due to surface contaminants, a second set of measurements on Ne was made a year after the first with a modified system. (See the section below for a description of these modifications.) The increased AC values for the second tube were confirmed by the additional measurements.

After these measurements had been completed and the second tube had been vacuum flashed at 2150°K a number of times, an electron micrograph was made of the surface of a small piece of this tube. This photograph is shown in Fig. 2D. A comparison of the two photographs (2C and 2D) shows in this case also the 2150°K vacuum flash produces drastic changes in the surface. However, after repeated flashing the

surfaces of the two different tubes appear very similar (2B and 2D). Evidently, the grain size in the surface is a function of flashing time and flashing temperature. AC values appear to be more dependent upon grain size than microscopic roughness.

IV. DISCUSSION OF RESULTS AND CONCLUSIONS

The original system for making the measurements described in 1975[1] has been considerably modified in the past year. In the original system, the sound source was moved by a magnet from outside the vacuum system. In the modified system this motion is accomplished by compressing a stainless steel bellows. The mercury vapor vacuum pumps have been replaced with an ion pump. The diaphrams on the transducers and the transducers themselves have been changed a number of times. Measurements have been made using several different frequencies. The EAC and TMAC values, while very sensitive to changes in the tube-wall surface, have been found to be independent of changes in the measuring system.

Three different tungsten surfaces have been studied. Measurements made on the original tube in 1974 have been compared with measurements made on this tube after it was highly oxidized and subsequently cleaned by flashing. Photographs made with the scanning electron microscope showed the surface to be greatly roughened by the oxidation process but its smoothness to be restored by flashing at 2150°K. AC values were changed little after the oxidation - and - subsequent - flash sequence.

Measurements have also been made on a second tube specified by the manufacturer as having $\frac{1}{2}$ the roughness of the first. Electron micrographs of this surface before and after flashing show that the

flashing process greatly increases the grain size. Accommodation coefficients for this second tube are somewhat larger than for the first. We attribute the difference to a smaller grain size in the second tube surface that was due to a shorter accumulated flashing time for this surface. The insensitivity of the AC values to microscopic roughness after the tubes have been flashed is not surprising when one examines the electron micrographs of the two surfaces (Fig. 2B and 2D). In these photographs, which were made at a magnification of x 10,000, the 5 micron roughness factor corresponds to about $\frac{1}{2}$ the width of the photograph.

The fact that the smoother surface (as specified by the manufacturer) gave the larger values for TMAC may be surprising in the light of results obtained by Steinheil, Scherber, Seidl and Rieger[3]. They observed that 5-μm grooves in an electrochemically polished copper (III) surface gave TMAC values greater than 1 for certain incident angles of a molecular beam. However, it is probably a mistake to try to compare their surface to the flashed tungsten surface. We can safely conclude from the larger EAC and TMAC values for the second, supposedly smoother tube that the diffused scattering of molecules from a surface is more sensitive to grain size than microscope roughness, and neither has nearly so large an effect as the adsorbed molecules on the surface.

ACKNOWLEDGEMENTS

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Legend for Figures

Fig. 1A & B. The theoretical reduced sound absorption (1A) and inverse reduced sound velocity (1B) plotted as a function of the reduced parameter r_ω. r' is 1.14. For curves A, EAC + TMAC = 0.6, and curves B, EAC + TMAC = 1.2. Curves numbered 1 are for EAC = TMAC and curves numbered 2 are for EAC = 0.2 TMAC. The figures show that while the sum of EAC & TMAC can be determined accurately from the acoustic data, individual values of the two are uncertain.

Fig. 2A & B. Scanning electron microscope photographs of a chemically deposited tungsten surface. In 2A the surface had been highly oxidized by a brief exposure to the atmosphere while at 2150°K. The oxide had then been removed by heating in a hydrogen atmosphere to 1400°K. Fig. 2B is micrograph of the surface after the oxide had been removed by repeated flashing at 2150°K in a vacuum.

Fig. 2C & D. Electron micrographs of the second tungsten surface with one-half the roughness of the first. In 2C the surface had been heated in a hydrogen atmosphere to 1400°K but had not been vacuum flashed. Fig. 2D is the same surface after repeated vacuum flashing at 2150°K.

Fig. 3A & B. The reduced sound absorption (A) and inverse sound velocity (B) in Ne plotted as a function of the reduced parameter r_ω. Points plotted as circles are for measurements made in the first tube after the oxide was removed by vacuum flashing. Points plotted as x's are measurements made with a second tube with surface specified to have one-half the roughness. The solid curves are theoretical values calculated using EAC and TMAC values determined for the first tube from measurements made before it was oxidized.

Fig. 4A & B. The reduced sound absorption and inverse velocity in He plotted as a function of the reduced parameter r_ω. Circles are for measurements made with second tube, the same one used for the measurements represented as x's in Fig. 3A & B. The solid curves are theoretical values calculated using EAC and TMAC values determined for the first tube from measurements made before it was oxidized.
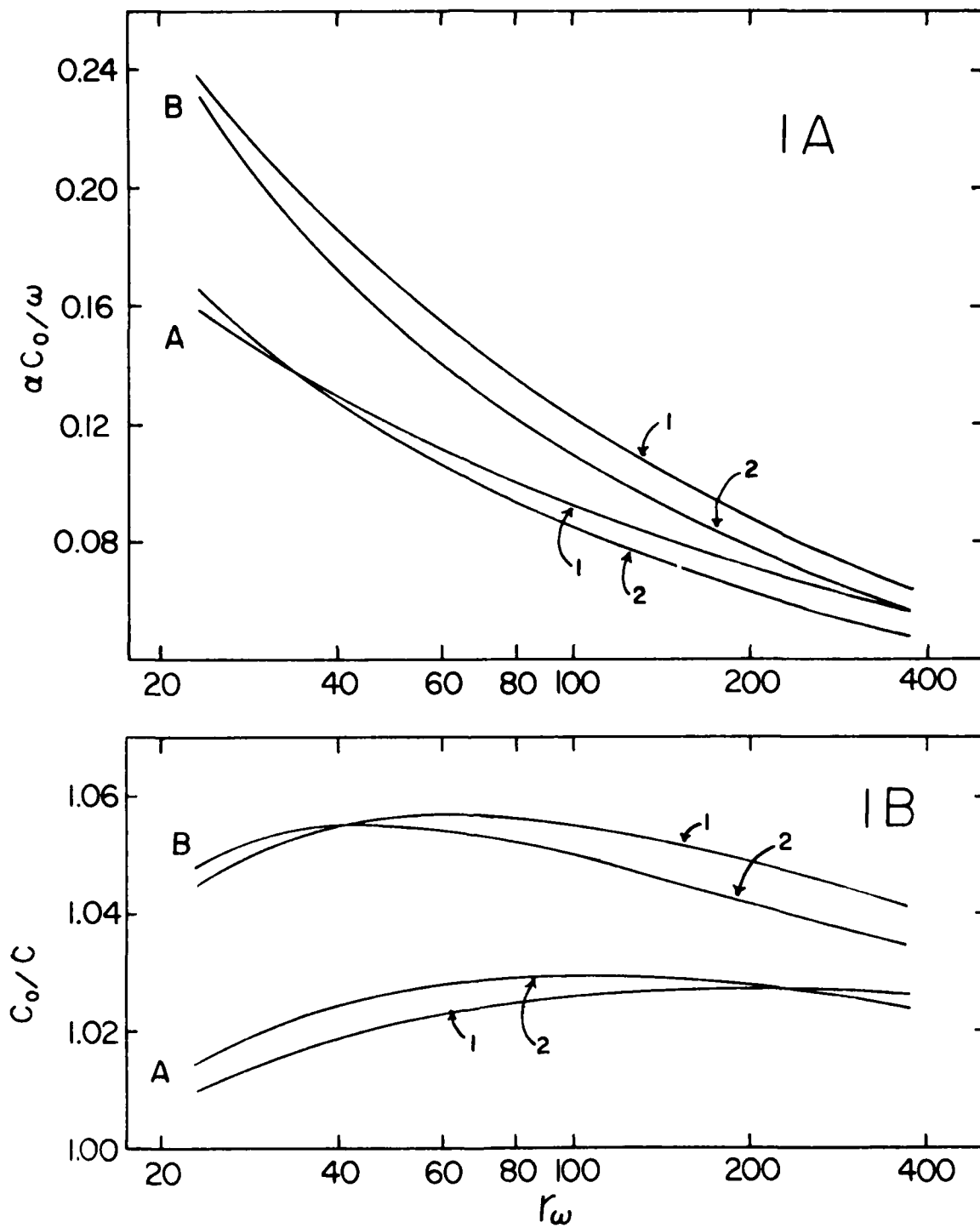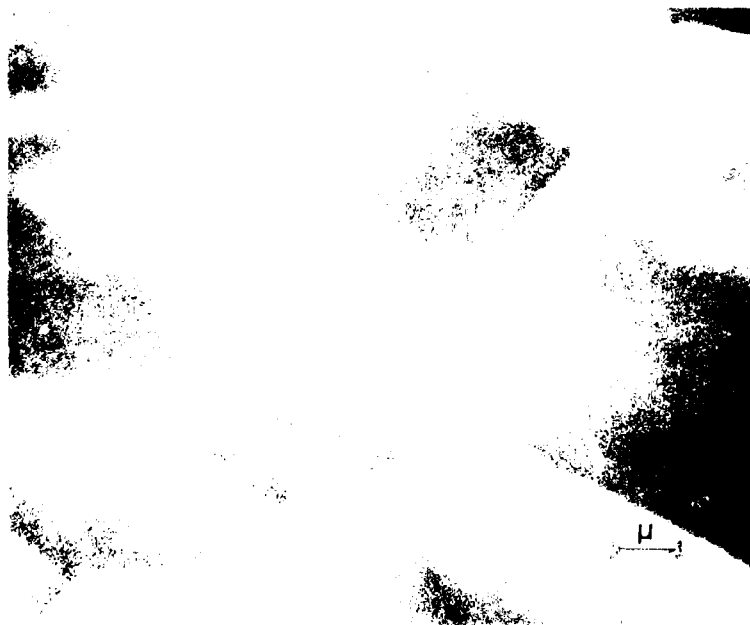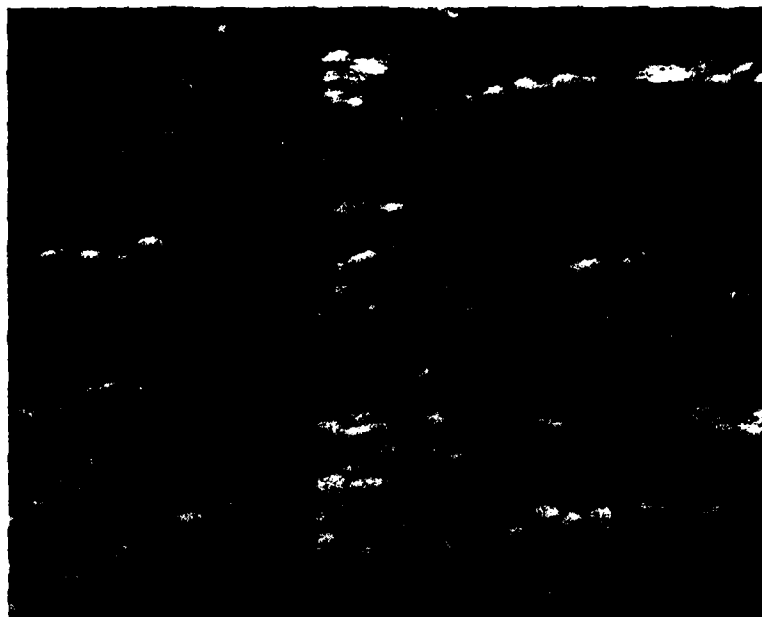
FIG. IA & IB
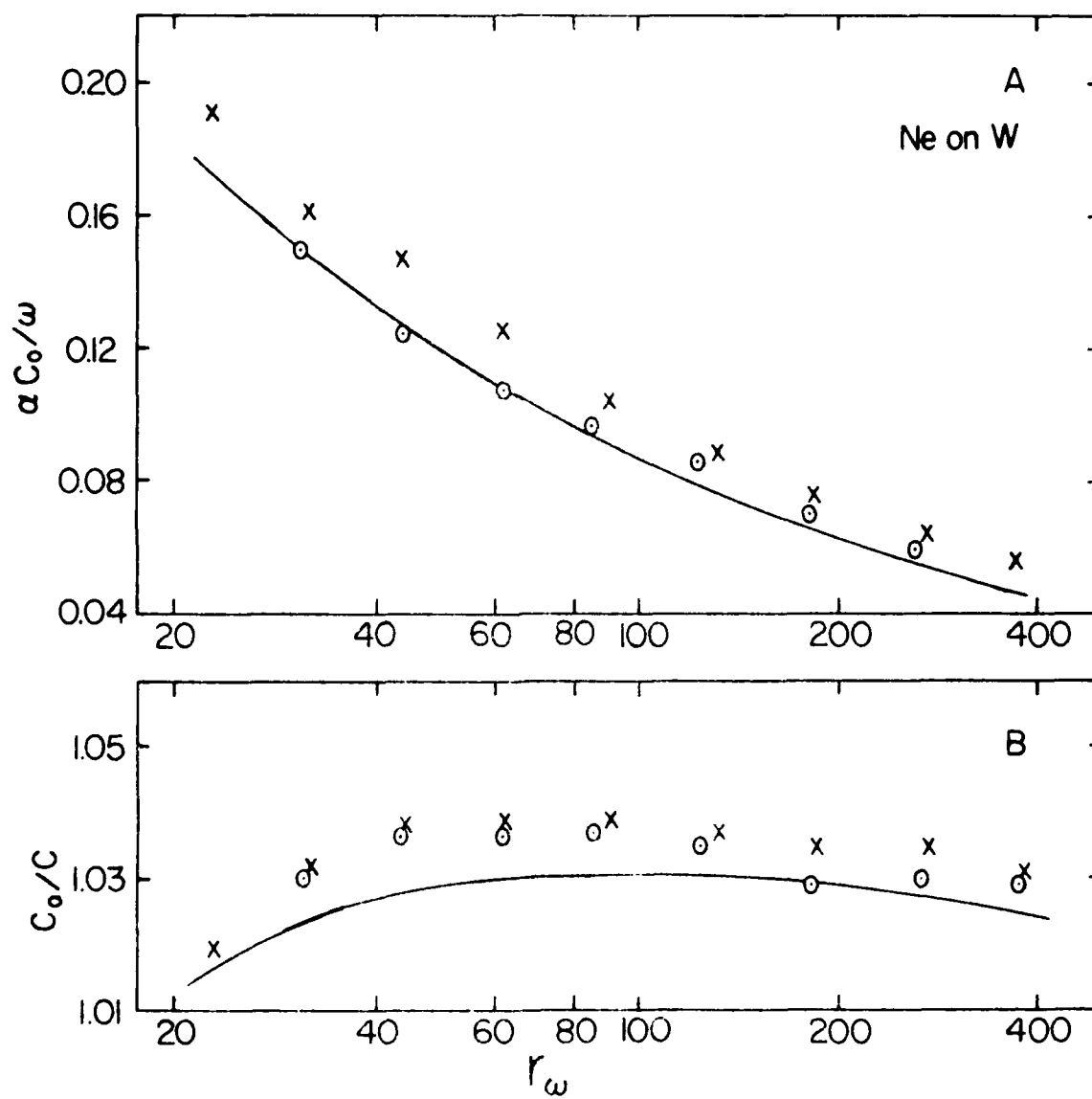
FIG 2 A

FIG 2 B

FIG 2 C
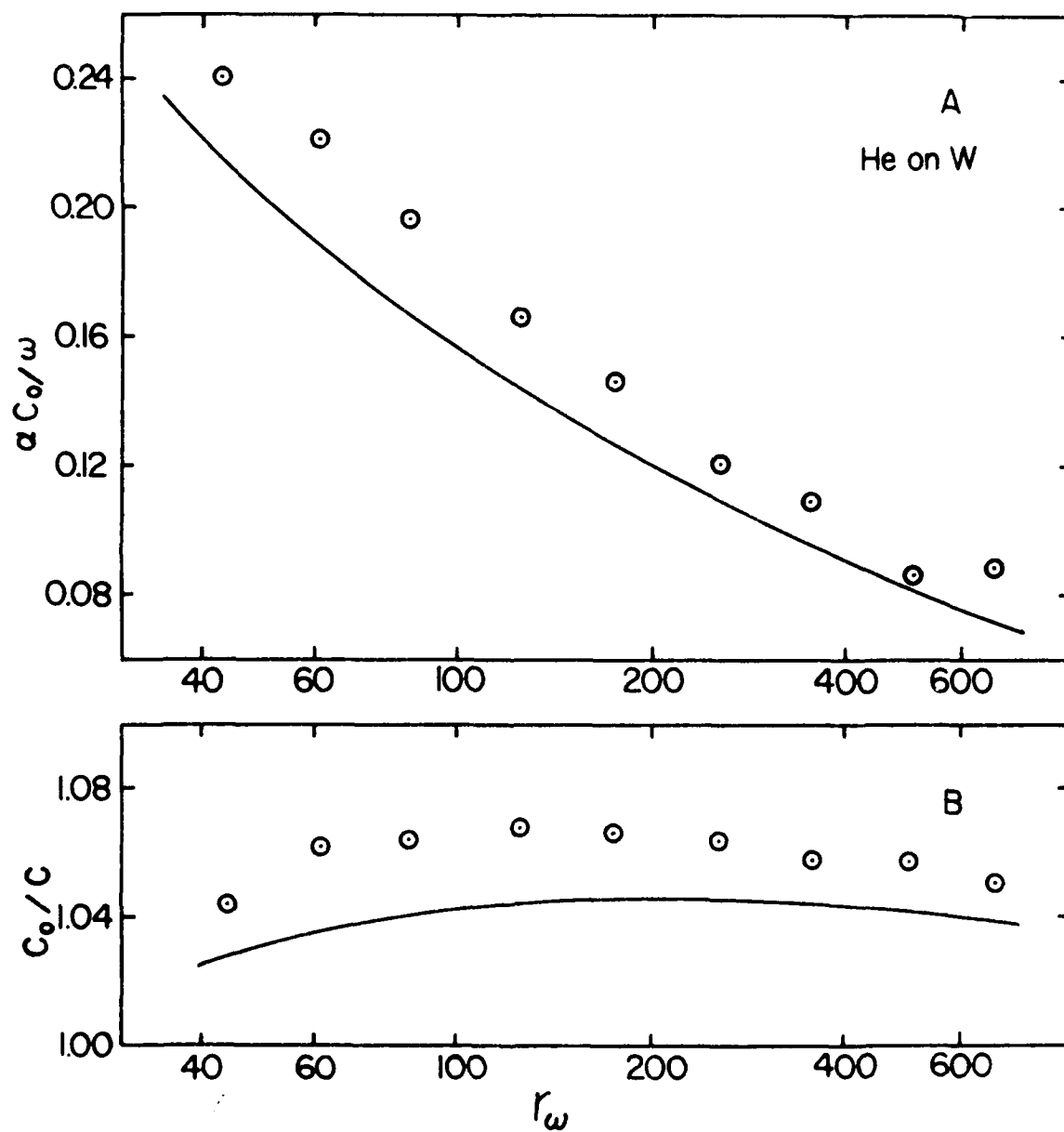

FIG 2D

FIG. 3 A & B

FIG. 4 A & B

PART II

ENERGY AND TANGENTIAL MOMENTUM ACCOMMODATION COEFFICIENTS ON GAS

COVERED TUNGSTEN

Abstract

The sum of the energy (EAC) and tangential momentum (TMAC) accommodation coefficients has been measured acoustically for Ne on W exposed to the following adsorbates: CO, CO_2, O_2, N_2, H_2O and D_2; for He on W with O_2 and D_2 as adsorbates; and for each of these adsorbates on itself on W. An effort has been made to infer separate values of EAC and TMAC from the measured values of their sum. Good agreement is obtained with EAC values obtained from thermal conductivity cell measurements if TMAC is assumed to have a value of 0.75 for He and Ne on all the gas covered surfaces and a value of 1.0 for all the adsorbates except D_2 on itself on W. The acoustical method which was used has the unique capability of determining AC values under gas dynamic conditions where the surface and the gas are at essentially the same temperature. For CO_2, since the acoustical measurements were made at frequencies far above the vibrational relaxation frequency, the EAC value obtained is for the translational and rotational energy only. The measurements in D_2 reveal rotational relaxation.

I. INTRODUCTION

Acoustic measurements reported in 1980[1] showed considerable difference in accommodation coefficients of He and Ne on a tungsten surface after it was exposed to a few Torr of oxygen and the same surface after an extended exposure to the atmosphere. This result suggested that it might be worthwhile to investigate the variation energy (EAC) and tangential momentum (TMAC) accommodation coefficients with different adsorbates on tungsten.

The measurements in D_2 were undertaken because molecular scattering experiments indicate that there is coupling between the rotational energy of the D_2 molecules and the phonons in the surface.[2] A second effect has also been studied, that of surface collisions causing transfer between rotational and translational energy within the gaseous molecule.[3] Therefore, some anomaly might be expected in the D_2 accommodation.

The measurements reported here are of an exploratory nature and show some of the capabilities and limitations of the acoustic method for measuring AC values.

II. PROCEDURE

The acoustic method of measuring the accommodation coefficients has been described earlier.[4,5] The surface studied here is the inside of a tungsten tube 0.953 cm inside diameter. The tube is the same one used in 1975[5] and 1980[1]. As discussed in the preceeding paper, it had been accidently heavily oxidized at the conclusion of the measurements reported in 1980. However, the oxidation process, after the oxides were removed by flashing, produced little change in the AC values for the clean tungsten surface.

Each time, before exposing the surface to the adsorbate, the tube was vacuum flashed repeatedly for 15 to 30 seconds at approximately 2150°K. In this flashing, since getter could not be used in the system, the pressure would generally rise briefly to the 10^{-6} Torr range, drop back to the 10^{-8} Torr range, and then rise slowly again to the 10^{-6} Torr range. During the flashing process, the system was left open to a 25 liter per second ion pump.

When using O_2, N_2, CO as adsorbates, the particular adsorbate gas was admitted to the system to a pressure of 100 mTorr and the tube flashed at about 2150°K in the presence of the adsorbate. Then the adsorbate gas was pumped out and measurements made with Ne or He on the gas covered surface. For oxygen, the pressure dropped from 100 to 20 mTorr in the flashing process. This change in pressure did not take place when flashing in the presence of N_2, D_2 and CO. For H_2O and CO_2, the tube was exposed to 10 Torr pressure without flashing.

Before making measurements with Ne, the system was pumped down to the 10^{-8} range. After the Ne measurements, the system was again pumped down and the adsorbate gas introduced for measurements with it. In making the measurements, the pressure was varied from 10 Torr to 0.7 Torr. The Ne and He used in making the measurements were passed over titanium at 900°C and through a liquid nitrogen trap to remove any surface contaminants.

The purpose in flashing the tube in the presence of the adsorbate gas was to allow it to replace any other surface coverage. Tests with O_2 and CO showed that additional exposure of the surface to pressure of adsorbate up to 10 Torr at room temperature did not change AC values a measurable amount. Also for D_2 and O_2, the same Ne AC values were obtained whether the surface was flashed in the presence of the gas or just exposed to 10 Torr pressure at room temperature.

III. DISCUSSION OF RESULTS

A. The experimental data

Fig. 1A and B shows a sample of the Ne sound absorption and velocity data. As in earlier papers, the real and imaginary parts of the reduced propagation constant are plotted against the reduced parameter, r_ω, which varies as the pressure divided by the frequency. $r^\prime$, the other reduced parameter upon which the reduced absorption and inverse velocity depend, has a value of 1.14 corresponding to a frequency in Ne of 17.8 kHz. The surface coverage for curves A and B are CO and N_2 respectively. The curves are theoretical, calculated with the computer-determined best value of EAC + TMAC.

In order to check the effect of the flashing process on the surface, measurements were made on the flashed surfaces before the series of measurements with the various adsorbates began and at their conclusion. These measurements are also plotted in Fig. 1A and B; the ones made before as filled circles and the ones after as filled squares. Some getter was present in the system when the data represented by the filled circles was taken. It is understandable that these data indicate somewhat lower AC values than the data represented by the filled squares. The latter were taken after the getter had been poisoned by the various adsorbates. It appears from these tests that the flashing process was removing surface contaminants. Therefore, flashing in the presence of the adsorbate should have produced the desired surface coverage.

Fig. 2 A and B shows samples of data taken using the adsorbate as the measuring gas. The curves are again theoretical values calculated using best-fit AC values.

B.   Tabulated values of TMAC and EAC

Table I gives the values of EAC plus TMAC which give the best simul-
taneous fit to velocity and absorption data. Also given in the table are
EAC values determined by Wachman using a thermal conductivity cell.[6]

As explained in the preceeding paper, the acoustical method measures
the sum EAC + TMAC much more accurately than either coefficient by itself.
This is especially true when the combined value of the coefficients is
large as it is in the present experiment.

For the case of Ne and He on the various adsorbates on W, we have
assumed a TMAC value of 0.75 for all adsorbates. When this value is sub-
tracted from the acoustically-measured value of EAC + TMAC, the resulting
EAC values are in suprisingly good agreement with values measured with
thermal conductivity cells. For the adsorbates on themselves on tungsten,
there is little thermal conductivity cell data with which to compare the
acoustic measurements. An assumption of unity for TMAC for N_2 on N_2 on W
gives a value of EAC close to the thermal conductivity cell value. We
have assumed a unity TMAC value for all the adsorbate gases except D_2.
It is a special case and is discussed below.

C.   Discussion of TMAC and EAC values

The following observations can be made from Table I:

1.   The relatively low AC values for Ne on N_2 on W confirm the previous
     observation that N_2 does not cover the W surface.[7]

2.   EAC values for Ne on N_2, CO_2, and O_2 on W; and for He on O_2 on W
     obtained acoustically (assuming TMAC = 0.75) agree within experimen-
     tal error with those obtained from thermal conductivity cell measure-
     ments.

3.   The ratio of the Ne to He EAC values for these gases on O_2 and D_2
     on W obtained acoustically (assuming TMAC = 0.75) is 2.6. This
     agrees with the value obtained from thermal conductivity cell

measurements on a number of other surfaces. (See note e in Table 1.)

4. For He and Ne on D_2 on W, there is a large discrepancy between the EAC expected from acoustical measurements and the value measure with the conductivity cell. The surface produced in our experiment by flashing D_2 in 100 mTorr of D_2 or exposing it to 10 Torr is obviously a different surface than that produced by exposure of the surface to the minute quantities involved in Wachman's experiments. In fact, in our experiments it was noted that a brief exposure of the tube to a surge of a few mTorr of D_2 when the getter was still active in the system prod ed little change from the clean surface A values. However, it should be noted as stated in 3 above, the Ne/He ratios obtained by the two methods are in agreement.

5. The discrepancy between the EAC values for CO_2 on CO_2 on W measured in the two ways may be due to the fact that the acoustical measurements were made far above the relaxation frequency. At these frequencies and pressures, the vibrational energy of the CO_2 gas is not being excited to follow the temperature variations in the sound wave. The vibrational temperature stays constant and equal to the wall temperature. Therefore, there is no net vibrational energy transfer between the wall and the surface. However, the vibrational energy exchanges which are taking place in equal number in both directions between the gas and the surface can contribute to randomizing the directions with which the molecules recoil from the surface. Therefore the value of TMAC should still be close to unity as in the other gases.

This means that the 0.72 value of EAC obtained acoustically is the EAC for translational and rotational energy only. The larger value obtained from thermal conductivity measurements implies EAC for vibration is greater than for translation and rotation. Such a large difference

could indicate that some of the translational-to-wall exchange is taking place through the vibrational modes. The EAC value of 0.72 for CO_2 is the only measurement known to the author of an accommodation coefficient for translational and rotational energy separate from vibrational energy.

D. Measurements with deuterium as the test gas

As explained in the introduction, the measurements in D_2 were undertaken because molecular beam experiments had indicated that the surface collisions were coupling the rotational energy of the molecules into either the vibrational energy of the solid surface or the vibrational energy of the molecule or both. The frequency over pressure range in which our acoustic measurements were being made corresponded to the onset of rotational relaxation. In this range then, as explained above in discussing the effect of vibrational relaxation in CO_2, the measured AC values should be frequency dependent. We have not been able to observe that frequency dependence. However, the D_2 measurements have yielded some interesting results. These results have been plotted in Figs. 3A and B, and 4. Most of the plotted points in these figures are the average of several measurements.

The manufacturer's specified isotopic purity for the D_2 was 99.5%. It was further purified in two different ways without noticeable difference in the results. In one method, the D_2 was absorbed in titanium at temperatures between 500 and 800°C and then subsequently desorbed at reduced pressure. In the second method, the D_2 was passed over the titanium at 950°C.

Before admitting the D_2 for the measurements, the sound tube was flashed in the presence of meshmetal getter at pressures in the 10^{-8}

Torr range. During a measurement, the D_2 was admitted at a rate suffi-
cient to balance the rate at which it was being absorbed by the getter
and, thereby, sufficient to hold the pressure constant.

Curves A in Figs. 3A and B have been plotted to show the effect of
relaxation in D_2. These are the curves resulting when the computer
searches for the best TMAC and EAC without including relaxation in the
analysis. The effect of relaxation in raising the reduced absorption
and lowering the inverse reduced velocity is clearly seen.

In order to account for relaxation, the computer program was modi-
fied to allow the specific heat entering the calculation to be frequen-
cy dependent and complex and given by the equation

$$C_v = C_\infty + \frac{C_i}{1 + iw\tau} \qquad 1.$$

C_i is the rotational part of the specific heat and, for a diatomic mole-
cule, is equal to the gas constant R. τ is the relaxation time and is
given by

$$\tau = \frac{1}{2\pi f_m} \cdot \qquad 2.$$

C_v is the specific heat at constant volume (2.5 R), C_∞ is that part of
C_v adjusting infinitely fast (1.5 R), and f_m is the frequency at which
the maximum in the sound absorption due to relaxation occurs. Accord-
ing to measurements by Stewart and Stewart,[8] and Winter and Hill,[9] f_m
should equal about 14 MHz per atmosphere. The fit to the experimental
data obtained when relaxation is included in this way is given by curves
B in the figures. This time the least squares fit to data give TMAC =
EAC = 0.56 when f_m is set equal to 14 MHz per atmosphere. Also shown
on Figs. 3A and B are curves, C, calculated assuming f_m = 14 mHz but
TMAC = 0.75 and EAC = 0.37. Note that the sum TMAC + EAC is the same

for both curves. The data does fit curve B better, but we may claim too much if we said it ruled out values of TMAC > EAC if their sum were equal to 1.12.

The rotational relaxation is not expected to be characterized by a single relaxation time as is implied in Eq. 1. However, the absorption data is not accurate enough to justify the more complicated multiple relaxation expression for the specific heat, especially since the transition rates for the individual rotational transitions are unknown.

In an effort to obtain the sound absorption due to relaxation from the experimental data, the theoretical absorption was calculated without relaxation assuming TMAC = 0.56 and EAC = 0.56 and these calculated values of the absorption subtracted from the measured values. The resulting "relaxation" intensity absorption per wavelength is plotted in Fig. 4. This method assumes the relaxation and classical effects are additive. When this assumption is tested by comparing the computer calculation used to get curve B in Fig. 3A with sum of the theoretical curve without relaxation and the relaxation absorption given by

$$\alpha\lambda = \frac{2f\, f_m\, A_m}{f^2 + f_m^2} \; ,$$

it is found to be good to within a few percent of the relaxation absorption up to the maximum in the relaxation absorption curve. For higher values of f/p the approximation fails, presumably due to a failure to allow for relaxation effects in the boundary layer. At 30 MHz per atmosphere, the measured value minus the numerically calculated absorption without relaxation is expected to give a value about 25% above the relaxation absorption curve. As is seen to be the case in Fig. 4, the experimental data does fall above the relaxation absorption curve in this

region by about this amount. In addition, the low experimental values
in the f/p range from 5 to 20 MHz/atm can be attributed to the multi-
ple-relaxation time process in the relaxation of the rotational energy.
When these two effects are taken into consideration, the deviation of
the experimental points from the relaxation curve in Fig. 4 is not sur-
prising.

E. Discussion of the D_2 results

From Figs. 3 and 4, we conclude that the D_2 measurements confirm,
within experimental error, the rotational relaxation frequency measured
by Stewart and Stewart in 1952, and Winter and Hill in 1967.

As discussed above, the acoustic measurements establish the sum
TMAC + EAC to within a few percent, but leave their separate values
uncertain. In D_2 the results do show a preference for TMAC = EAC over
the more often encounter results of TMAC considerable bigger than EAC.
It is interesting to note that Weinberg and Merrill[2] measure a "diffuse
fraction" of 0.52 and 0.55 for D_2 scattering from single crystal tung-
sten at 625 and 775°K, respectively. They conclude that surface dis-
order is important in inducing rotational energy exchange with the sur-
face. The best fit to our data gives TMAC and EAC both equal to 0.56
for polycrystalline tungsten with a molecular layer on it (as deter-
mined by the He and Ne measurements). The added disorder of our poly-
crystalline surface may be compensating for its lower temperature to
give a value for the accommodation coefficients comparable to Weinberg
and Merrill's.

If the acoustically preferred values of .56 and .56 for TMAC and EAC
are correct, then 56% of the molecules are scattered diffusely and all of
those so scattered have been energy accommodated. This is quite different from

monoatomic gases where, from the same surface, a significant fraction of the molecules that are scattered diffusely have made elastic collisions. The relatively large value of EAC and small value of TMAC as compared to He substantiates the conclusion that a significant part of the heat transfer at the surface is occurring through the rotational motion of the molecule.

It should be noted that vibrational relaxation was included in the analysis of the CO_2 measurements in the same way that rotational relaxation was included in the analysis of the D_2 data. However, in the CO_2 case the measurements were made at frequencies far above the relaxation region. In that case, the specific heat "seen by the sound wave" was essentially 5/2 R.

IV. CONCLUSIONS

By comparing acoustic measurements of TMAC + EAC with thermal conductivity cell measurements of EAC, we have concluded that TMAC is approximately equal to 0.75 for both Ne and He on all adsorbates on W measured.

For the adsorbates on themselves on tungsten, a better choice for TMAC seems to be unity. The EAC values then range from 0.32 for H_2O on H_2O on W to 0.8 for O_2 on O_2 on W. The EAC values appear to be more of an indication of the surface coverage by the adsorbate than of its energy transfer efficiency.

The D_2 acoustical measurements, when analyzed assuming a rotational relaxation frequency of 14 MHz per atmosphere, indicate TMAC = EAC = 0.56, with the sum, TMAC + EAC = 1.12, much more certain than the individual values. The relatively large value of EAC and small value of TMAC would confirm molecular beam results indicating a coupling between the rotational motion of the molecule and the surface states.

In the case of CO_2, the value of EAC obtained (0.72) is for translational and rotational energy only and is the only such measurement known to the author. A much bigger value of EAC (0.99) obtained from thermal conductivity cell measurements would indicate that the vibrational motion of the molecule plays a role in transferring translational energy to the surface.

ACKNOWLEDGEMENTS

Table 1. Energy and tangential momentum accommodation coefficients for various gases on gas covered tungsten.

Gas	Surface	TMAC + EAC from Acoustical Measurements	TMAC	EAC	EAC(a) from Thermal Conductivity
Ne	N_2 on W	0.92	0.75	0.17	0.18(b)
Ne	CO_2 on W	0.96	0.75	0.21	0.28(c)
Ne	CO on W	1.16	0.75	0.41	
Ne	O_2 on W	1.20	0.75	0.45	0.41
Ne	H_2O on W	1.16	0.75	0.41	
Ne	D_2 on W	1.20	0.75	0.45	0.12
He	O_2 on W	0.92	0.75	0.17	0.19
He	D_2 on W	0.92	0.75	0.17	0.046
N_2	N_2 on W	1.68	1.00	0.68	0.64
CO_2	CO_2 on W	1.72	1.00	0.72	0.99
CO	CO on W	1.44	1.00	0.44	
O_2	O_2 on W	1.80	1.00	0.80	
H_2O	H_2O on W	1.32	1.00	0.32	
D_2	D_2 on W	1.12	0.56	0.56(d)	0.23

(a) From Y.H. Wachman, Ph.D. thesis, University of Missouri, 1957, pp. 157,158, with the following notes.

(b) inferred from Wachman's He measurement (See p. 123 of his thesis.) and from Van Cleave, Trans. Faraday Soc. 34, 1174 (1938).

(c) inferred from Wachman's He value of 0.11 assumming a Ne/He ratio of 2.6. (See L.B. Thomas, in Fundamentals of Gas Surface Interaction, edited by H. Saltzburg, J.N. Smith, Jr., and M. Rogers (Academic Press, New York, 1967), p. 362.

(d) from best fit to acoustic data reported here.

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Legend for figures.

Fig. 1A and B. Reduced sound absorption and inverse sound velocity in Ne plotted as a function of the reduced parameter, r_ω. The open squares are for measurements made after the tube wall had been exposed to CO. For the open circles, it had been exposed to N_2. The curves drawn through these points were calculated using EAC + TMAC values given in Table 1. The filled squares and circles are for measurements made with the surface vacuum flashed. The circles are for measurements made at the beginning and the squares for measurements made at the conclusion of the measurements with the various adsorbates.

Fig. 2A and B. Reduced sound absorption and inverse sound velocity in adsorbate gases plotted as a function of the reduced parameter, r_ω. The curves were calculated using EAC + TMAC values given in Table I.

Fig. 3A and B. Reduced sound absorption and inverse sound velocity in D_2 plotted as a function of the reduced parameter, r_ω. Curves A are the theoretical curves calculated assuming no relaxation. Curves B are for EAC = TMAC = .056. Curves C are for EAC = 0.37 and TMAC = 0.75.

Fig. 4. Sound intensity absorption per wavelength as a function of frequency divided by pressure. The theoretical curve assumes rotational relaxation with a single relaxation time with the frequency of maximum absorption equal to 14 MHz per atmosphere.
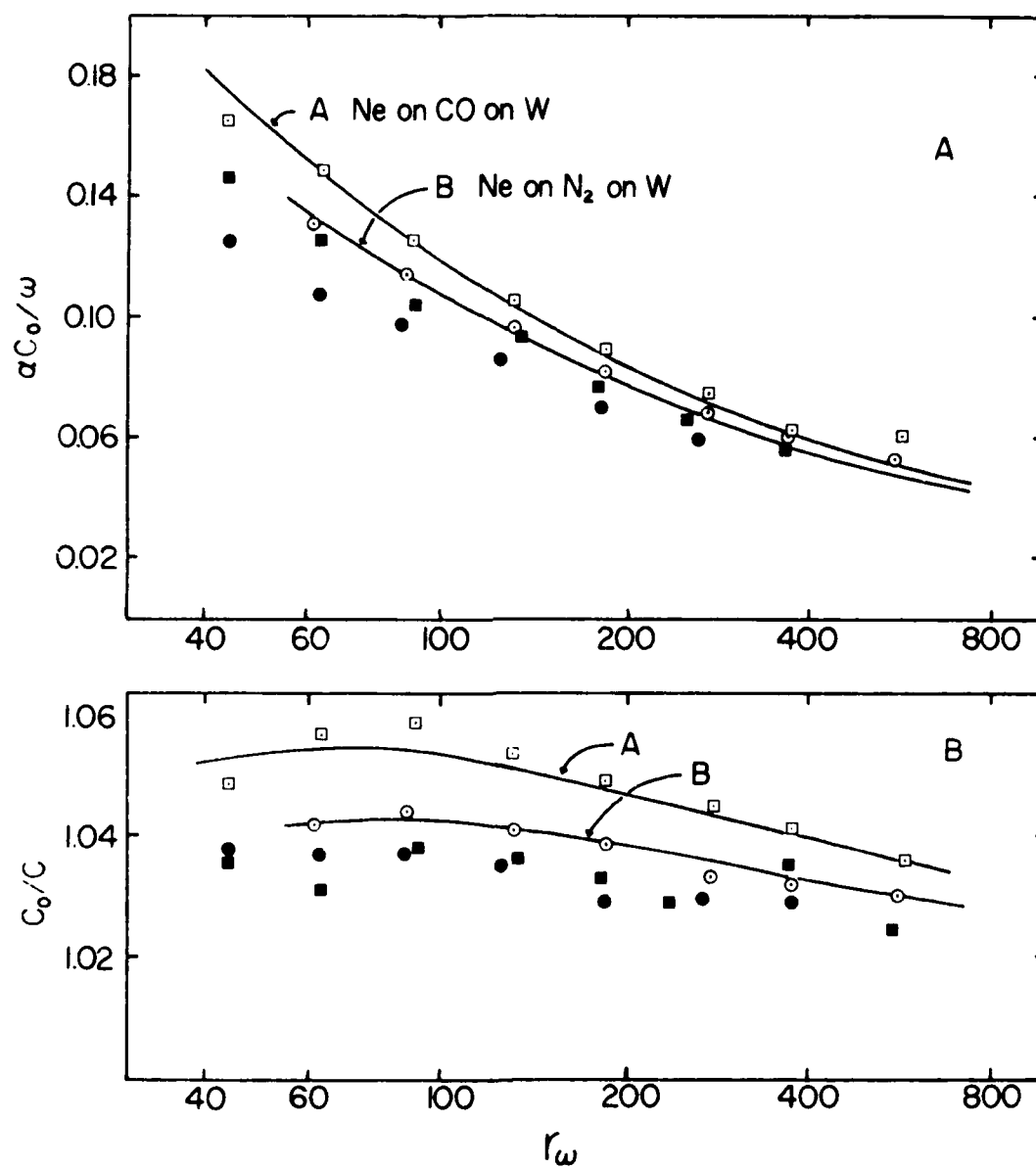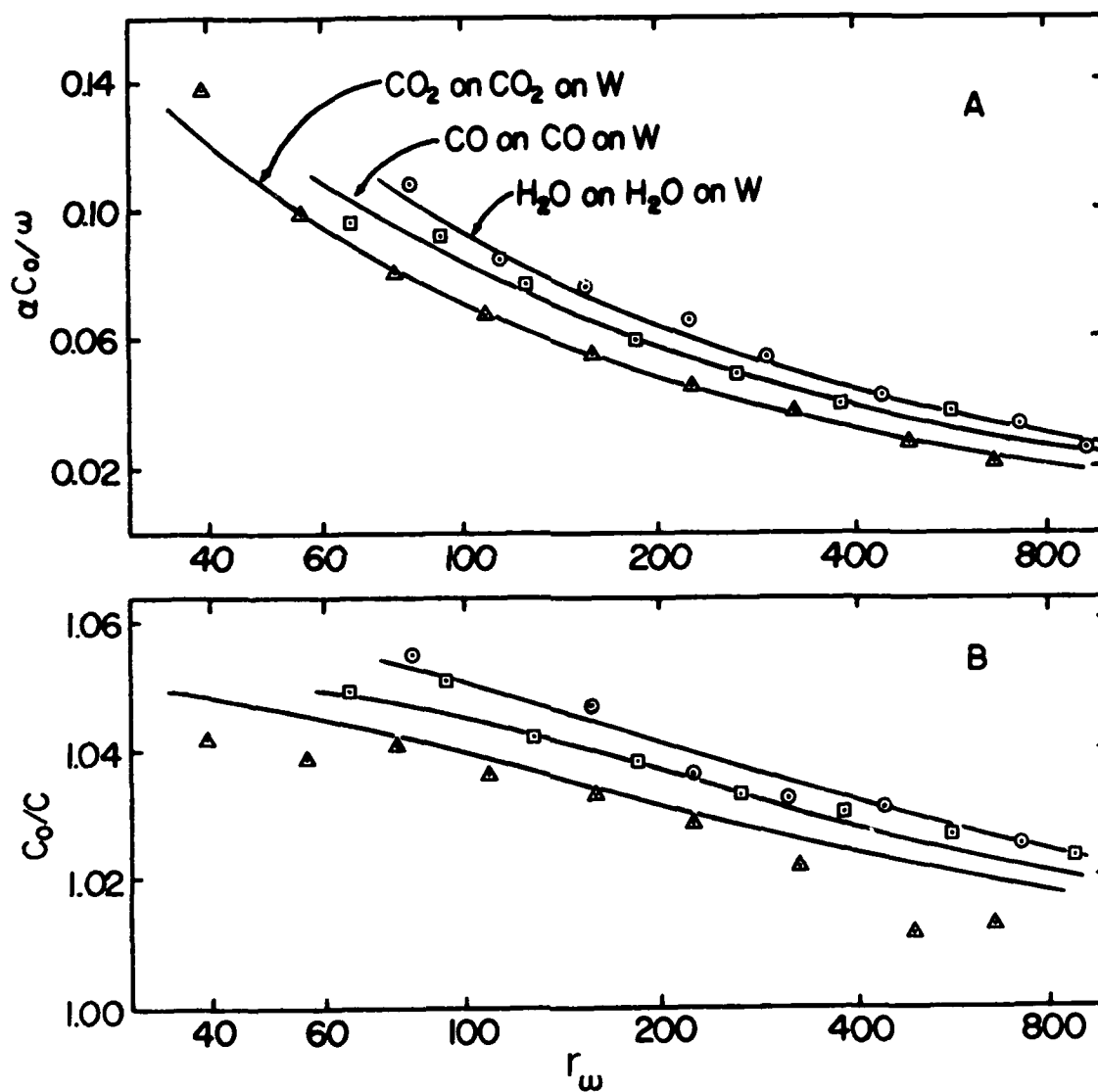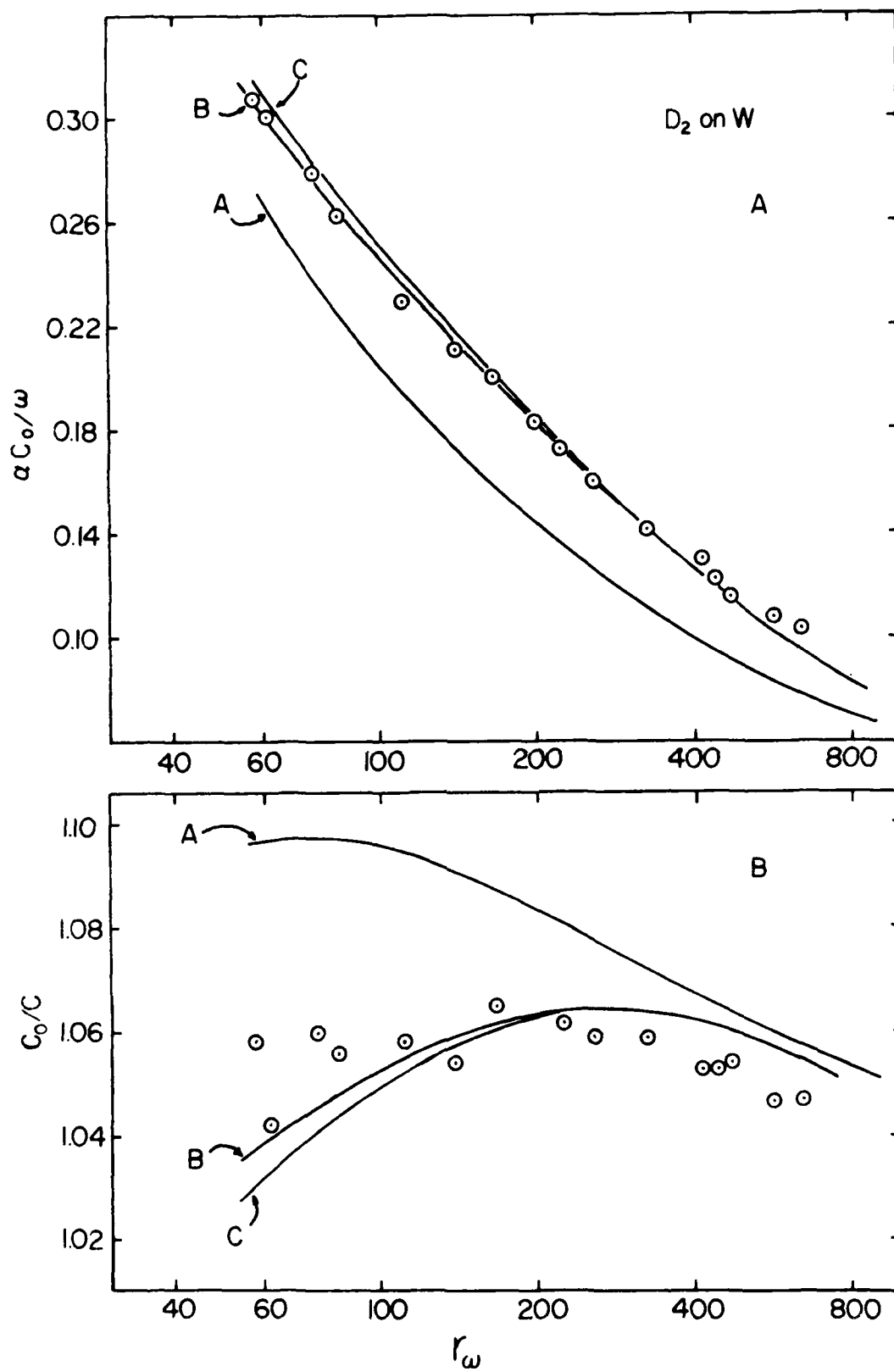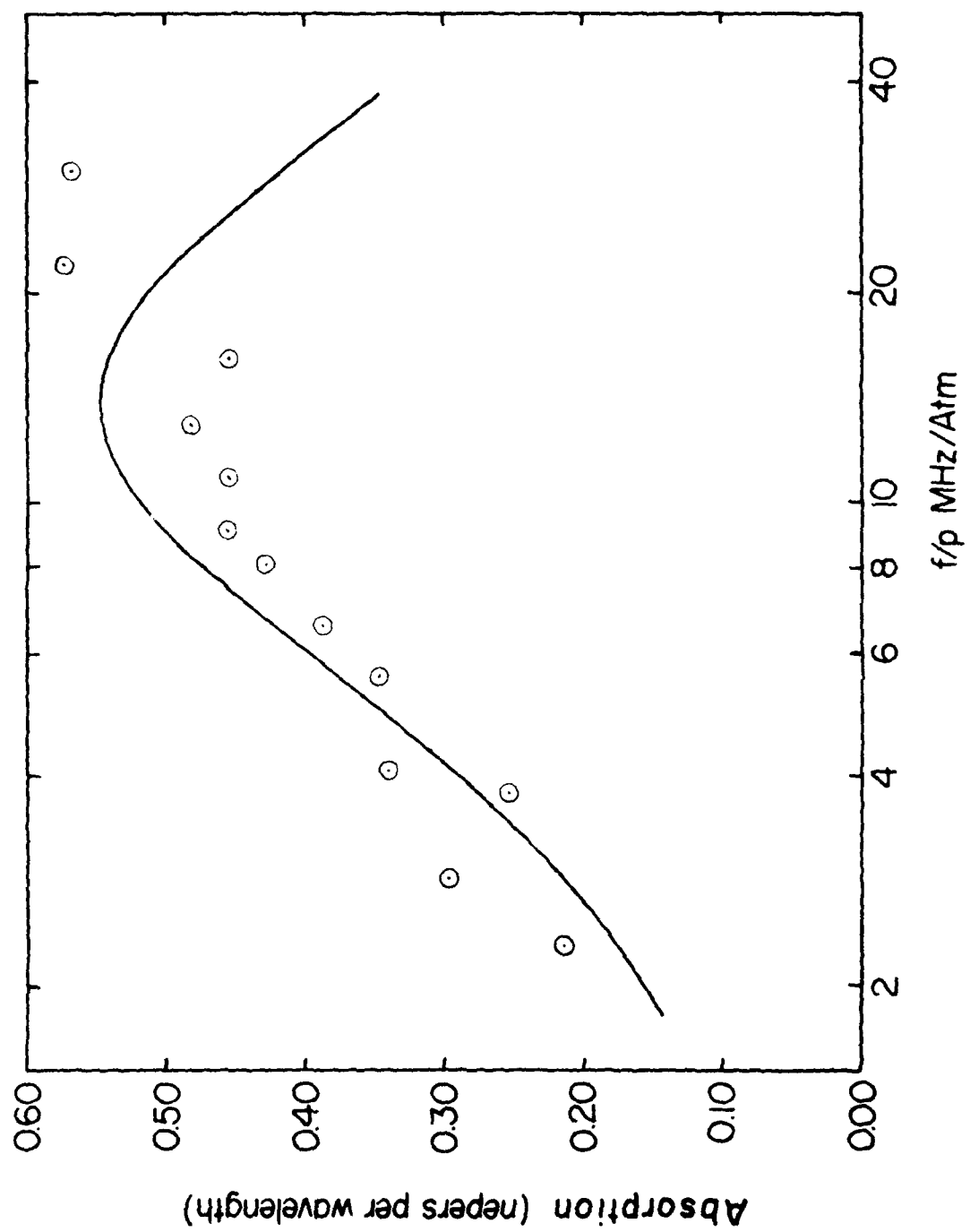
FIG. I A & B

FIG. 2 A & B

FIG. 3 A & B

FIG. 4

Absorption (nepers per wavelength)

0.60 0.50 0.40 0.30 0.20 0.10 0.00

f/p MHz/Atm

2   4   6   8   10   20   40